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Fibre–matrix interface effects in asbestos–cement composites

S. A. S. AKERS
Amiantus Centre, CH-8867 Niederurnen, Switzerland

G. G. GARRETT
Department of Metallurgy, University of the Witwatersrand, Johannesburg, Republic of South Africa

The microstructure and failure mode of the fibre–matrix interfacial region in asbestos–cement composites have been investigated, primarily by scanning electron microscopy. Processes of bonding and debonding are shown to be complex, involving a variety of mechanisms. Mutual interlocking has been observed between asbestos fibrils and calcium silicate hydrate needles, whereas fibre pull-out occurs primarily through matrix failure adjacent to the interface, together with some interfibre separation.

1. Introduction

The poor tensile properties and ostensibly brittle characteristics of the cheap inorganic materials used principally in the building industry have long represented the major limitation to their even more widespread application as engineering materials. However, their low cost of manufacture, particularly on an energy basis [1] presents definite advantages, and numerous schemes involving microstructural manipulation have been suggested over the years to improve both strength and toughness. Prime amongst these has been fibre-reinforcement, and the object of this paper is to report on aspects of a study which aimed to examine the factors influencing the mechanical properties of one of the industrially most successful of the fibre-reinforced cement-based materials, asbestos–cement.

Asbestos–cement composites have been in use for well over seventy years, but with current limited global reserves coupled with a perceived health hazard, considerable effort has been devoted in recent times to finding suitable alternative fibres to asbestos. However, it has been realized that such an objective is hardly straightforward since, in addition to being relatively inexpensive, asbestos fibres have certain inherent properties which many replacement fibres do not possess. For example, they show high resistance to chemical attack, have excellent mechanical properties (tensile strengths ~ 0.5 to $1.0\,GN\,m^{-2}$ and elastic moduli $\sim 150\,GN\,m^{-2}$) and, in addition, are fire resistant. Furthermore, the "wetting" of asbestos fibres in the presence of fresh cement, i.e. the ease with which cement adheres to the fibre surface, is such that the preparation of the composite presents few production difficulties.

2. Mechanical properties and the fibre–matrix interfacial bond

Microstructural understanding is likely to be useful in any substitution programme, and in fibre composites the fibre–matrix interface represents one of the most vital regions governing material performance. The interfacial bond itself can be physical or chemical in nature, or a combination of the two, as determined by the fibres and the matrix. Thus, it has been reported that for glass fibre–cement composites the bond is partly chemical in nature due to the nucleophilic attack of OH^- ions on the Si–O bond [2]. For steel fibres in cement it has been suggested [2] that diffusion of ions across the interface can occur, resulting in a partial chemical bond. However, there is considerable evidence to the contrary [3, 4], suggesting that the bond is essentially mechanical, i.e. arising from purely frictional shear transfer. For very old (50 years) asbestos–cement composites,

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on the other hand, analysis has indeed indicated that a reaction between calcium hydroxide and chrysotile asbestos fibres has taken place [5].

In simplistic terms, a strong interfacial bond is generally desirable for maximum composite strength, in order to utilize the full reinforcing capacity of the fibres. On the other hand, a weaker interfacial bond can have advantages with regard to composite toughness, either by promoting crack tip blunting by interface delamination and/or though an increased work of fracture by fibre pull-out after fibre breakage.

The mechanical behaviour of a fibre composite is therefore directly related to the nature and properties of the fibre–matrix interface and it is clear that, in order to achieve a strong yet tough material, a compromise must be sought. One obvious way of overcoming this problem would be to produce a composite with a combination of weakly and strongly bonding fibres. However, this is not as elementray as it might at first appear, since the interfacial bond in cement-based fibre composites can be affected by a number of variables such as the water/cement ratio, porosity, chemical composition of the fibres and matrix, as well as fibre surface irregularities.

This paper, then, considers in some detail the nature and properties of the interfacial zone in asbestos–cement composites and the corresponding influences on the mechanical properties of the composite.

3. Experimental details

Compositional and fractographic studies of the asbestos–cement interfacial region were carried out by scanning electron microscopy, using a Cambridge S-180 SEM equipped with energy dispersive X-ray analysis facilities. Small samples were cut from the fracture surfaces of both laboratory and production line sheets (to compare the consistency of the results so obtained), which had been broken in flexure. All fracture surfaces were washed in acetone and placed in a vacuum desiccator in order to arrest the hydration process and avoid contamination by carbon dioxide from the atmosphere. Individual fibre bundles were also examined, utilizing appropriate mounting and correction procedures.

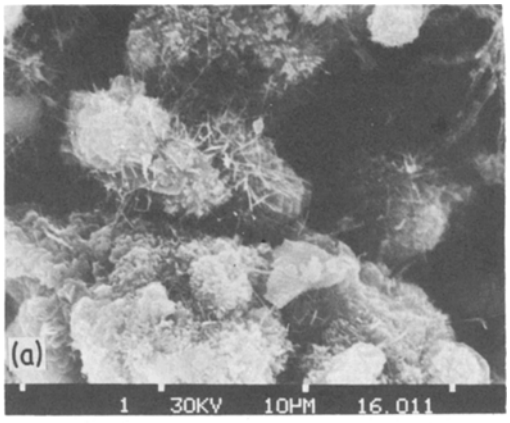
The determination of composition gradients adjacent to interfaces, involving the comparison of elemental distributions by semi-quantitative X-ray analysis, must be carried out with due caution: the technique can be subject to criticism if the operator is unaware of certain shortcomings in attempting to ensure acceptable statistical precision. Thus, Diamond *et al.* [6] have documented precautionary measures which should be adhered to in the investigation of rough surfaces, such as cement fractures, by X-ray analysis.

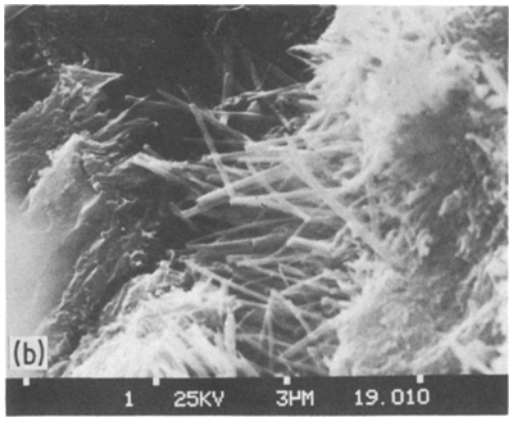
4. Results and discussion

For fibre composite materials where no chemical bond is involved, and where, on a scale appropriate to the interfacial region, microstructural homogeneity predominates, conventional concepts of load transfer between fibres and matrix often invoke some form of frictional shear. However, as will become evident, this cannot justifiably be considered the case for a cement matrix. Thus in order to examine the binding mechanism between the cement and the asbestos fibres, it is necessary first to consider the morphology of the matrix itself, in the hydrated form.

The hardening of Portland cement is primarily due to the hydration of the constituent di- and tri-calcium silicates. A wide variety of corresponding microstructural forms have been identified over the years, and variously described as: needles, fibres, cigar-shaped sheets, plates, crumpled sheets or foils, tabulated structures, thin sheets, spicules, spherulitic particles and rosettes [7]. Indeed, very recently the origins of, and influences controlling, such structures have been the subject of enthusiastic debate [8, 9] beyond the scope of this paper. However, prime amongst the structural forms of the hydrates is that of needles or tubular fibres (Fig. 1), which are widely considered to play a dominant role in the strength development of hydrating cement. Thus, these needles can be seen to interlock and bond together adjacent cement particles (Figs. 1a and b), providing the basis for the mechanical strength of the material. They can also grow across voids in the structure, resulting in an overall decrease in porosity, as well as act to inhibit crack initiation at such voids; furthermore, they can bridge microcracks formed during curing, Fig. 1c, again leading to local strength improvements.

Turning attention to the asbestos fibres, an investigation of the microstructural implications of one of the production line processing treatments, known as "fiberizing", has shown that this involves the progressive opening of asbestos fibre bundles, Fig. 2. In a cement matrix, the fine





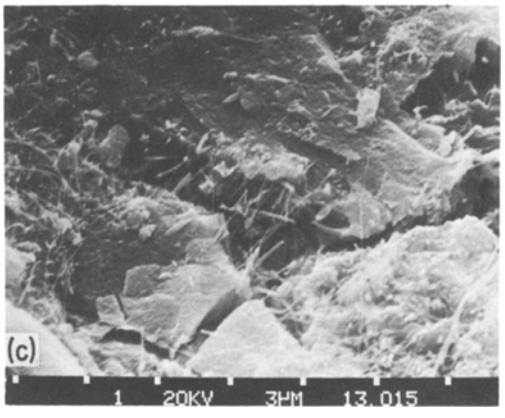


Figure 1 Calcium silicate hydrate of the needle morphology which interlocks and binds cement particles together, (a) and (b), as well as microcracks formed during curing (c).

asbestos fibrils, Fig. 2c, will interlock with the cement hydrate needles which can be seen, Fig. 1b, to be of similar dimensions. This interlocking, shown in Fig. 3, is obviously beneficial to the strength of the composite, and would appear to represent an interesting new variation to the more conventional models of load transfer in fibre reinforcement. Even in the case of large fibre bundles, there is reason to believe that such an interlocking mechanism may contribute to the strength of the bond between a fibre bundle and the matrix. Thus Fig. 4 shows evidence of the presence of fine asbestos fibres, of dimensions again similar to the needle-like cement hydrate form, on regions of the all-important surface of the bulk fibre bundle.

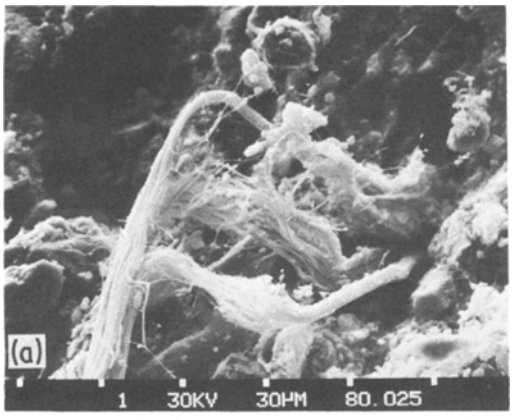
Mechanical property measurements have leant support to the interlocking mechanism, since significant improvements in flexural strength have been observed with well-fiberized specimens cured under water (i.e. optimized interlocking) when compared with those subject to less fiberization and air cured; single fibre (bundle) pull-out tests also confirm such improvements, Table I.

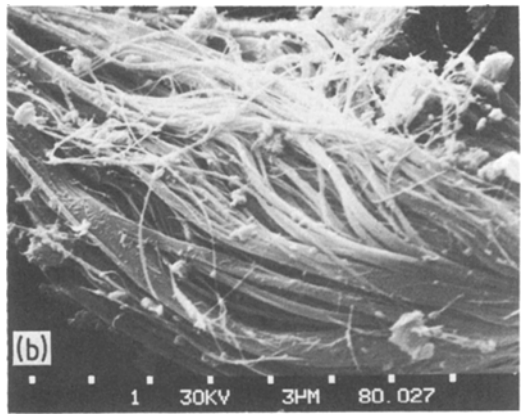
It should be noted, however, that the interlocking of fine asbestos fibrils and silicate hydrate needles would appear to be but one mechanism for interfacial bonding in asbestos–cement. Since typical industrial asbestos–cement consists of a very wide range of fibre lengths and diameters, it is also important to investigate the interfacial region in relatively large fibre bundles, i.e. of diameters in excess of $\sim 5\,\mu m$.

Using X-ray analysis on a typical fibre bundle which has been pulled out of the cement matrix (Fig. 5a), there are obvious traces of small cement particles adhering to the fibre bundle. Since the chrysotile asbestos fibres used do not contain calcium, from a calcium elemental distribution map of the fibre bundle, Fig. 5b, it is clear that a thin film of cement is adhering to the fibre bundle, as has previously been reported by Majumdar [2]. In other words, failure has taken place in the cement *adjacent* to the interface, as distinct from

TABLE I The influence of degree of fiberization and curing procedure on mechanical strength. (All measurements in $N mm^{-2}$.) The "spinning" operation, involving rigorous paddle stirring of the asbestos with water, separates and opens the fibre bundles: long spinning times will have well-opened fibre bundles in comparison with short spinning times.

	Flexural tests		Single fibre pull-out tests
	Short spinning (15 min)	Long spinning (60 min)	
Air cured	43	40	1.8
Water cured	44	51	2.4





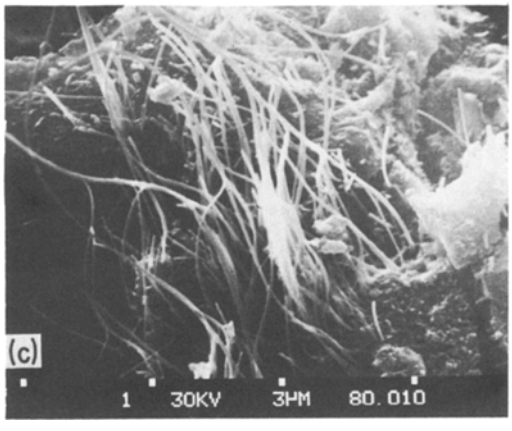
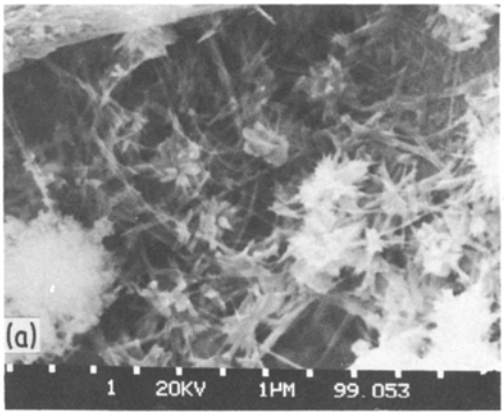


Figure 2 Progressive opening of fibre bundles during the fiberizing treatment.

at the interface itself (in which case the fibres would not be expected to still be covered with a cement layer).

Now it has been suggested [10] that local regions adjacent to the interface in fibre-reinforced cement products could be enriched in calcium hydroxide, a by-product of the cement hydration process generally considered to be a weak, readily fractured phase [11] with a correspondingly marked deleterious effect on the strength of the cement in the interfacial zone. Thus Pinchin and Tabor [10] reported a calcium hydroxide enriched zone $\sim 10\,\mu m$ from the interface in steel fibre-reinforced cement, and suggested that this enrichment may be regarded as a localized zone of weakness within the matrix where interfacial debonding could initiate and take place preferentially. Similarly, Morris and Garrett [4] found calcium hydroxide enrichment $\sim 30\,\mu m$ from such steel fibre interfaces and proposed that voids formed adjacent to the fibres during vibration compaction promote the formation of a weak, calcium hydroxide-rich zone close to the fibre. The presence of calcium hydroxide has also been reported in voids near the interface of glass fibre-reinforced cements [12–14], although no specific mention was made of enrichment at the interface



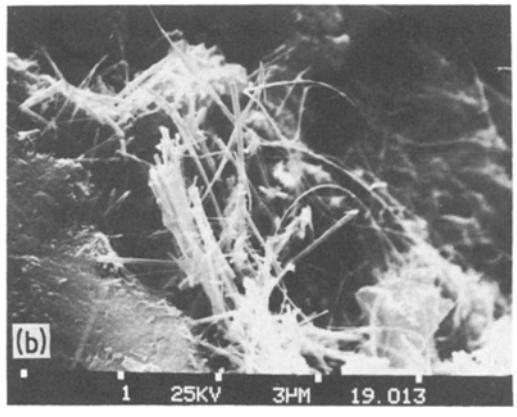


Figure 3 Interlocking of fine asbestos fibres with calcium silicate hydrate needles.

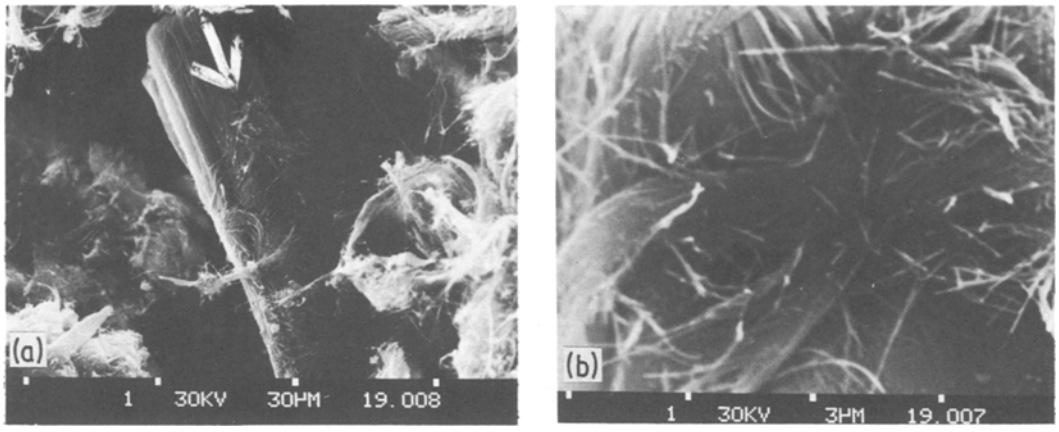


Figure 4 Fine fibrils found on the surface of large fibre bundles; (b) is the region arrowed in (a) at higher magnfication.

itself, or of the corresponding effect on the strength of the composite. It is clear, however, that if such regions do indeed exist, they will present a limit to improvements which might accrue from fibre processing, since the failure characteristics of the composite will effectively be controlled by this "weak link".

If debonding initiates at a weak calcium hydroxide-enriched zone within the matrix and away from the interface, a higher value would be expected for the calcium/silicon ratio on the surface of a pulled-out fibre bundle, when compared with that obtained from the bulk. However, line scan X-ray analysis carried out at, and away from, the interface of exposed fibre bundles, suitably corrected for the silicon content of the asbestos fibres, indicates that there is no such calcium hydroxide-enriched zone, Fig. 6. This result is consistent for both laboratory and production line specimens, although in the latter case, there is a higher (still constant) calcium/silicon ratio which appears to be due to the much higher calcium ion concentration in the water used in production sheet manufacture.

It could also be argued that if some weak, calcium hydroxide-rich zone did occur, calcium hydroxide crystals could dislodge from the cement adhering to the fibre bundle during pull-out, leaving behind the majority of the calcium hydroxide in the residual trough. For this reason line scan analyses were also performed in, and at various distances from, a cement trough out of which a single fibre bundle had been extracted. Again (Fig. 6) no zone enriched in calcium hydroide is evident.

At higher magnifications, line scan analyses proved to be unrepresentative and, at certain distances from the interface, increases in the

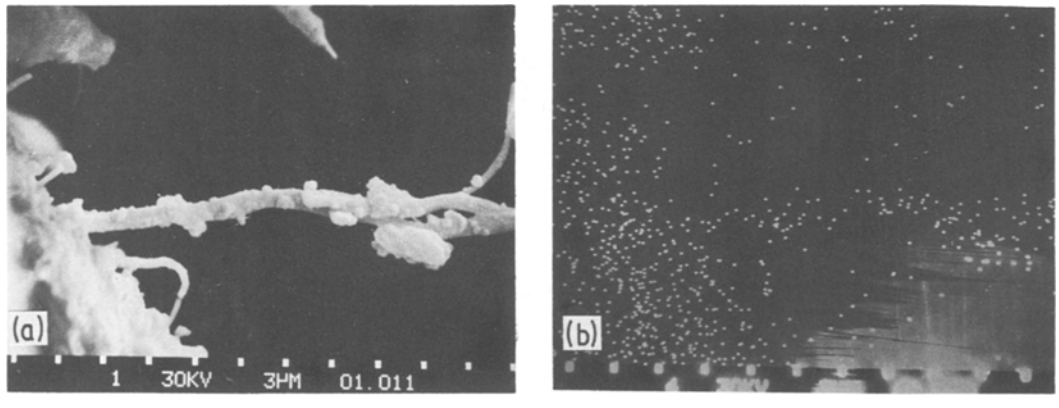


Figure 5 (a) Typical fibre bundle pulled out of a cement matrix, still covered with a layer of cement. (b) A Ca$K\alpha$ elemental distribution map of this fibre bundle confirms the presence of calcium, which could only have come from the cement left adhering to the bundle.

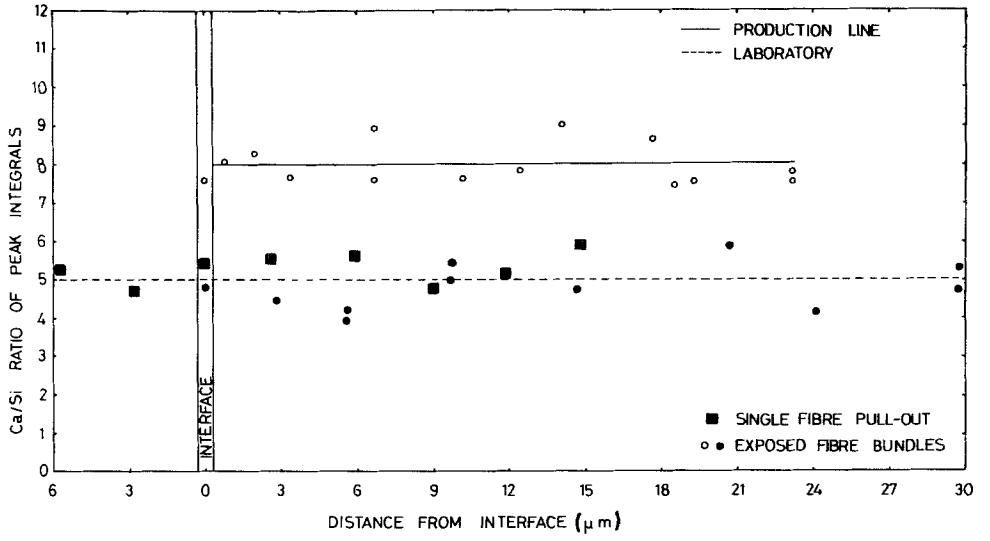


Figure 6 Corrected Ca/Si ratios of the fibre–cement matrix interfacial region, indicating no $Ca(OH)_2$ enrichment.

calcium/silicon ratio by a factor of 2 above the bulk value were recorded, Fig. 7. Elemental distribution mapping, Fig. 7, confirmed the presence of individual calcium hydroxide crystals in such areas. Such irregularly occurring calcium hydroxide crystals in the interfacial region will obviously present localized weak zones for preferential initiation of cracking. However, in general terms, this investigation has shown that in asbestos–cement there is no evidence of a struc-

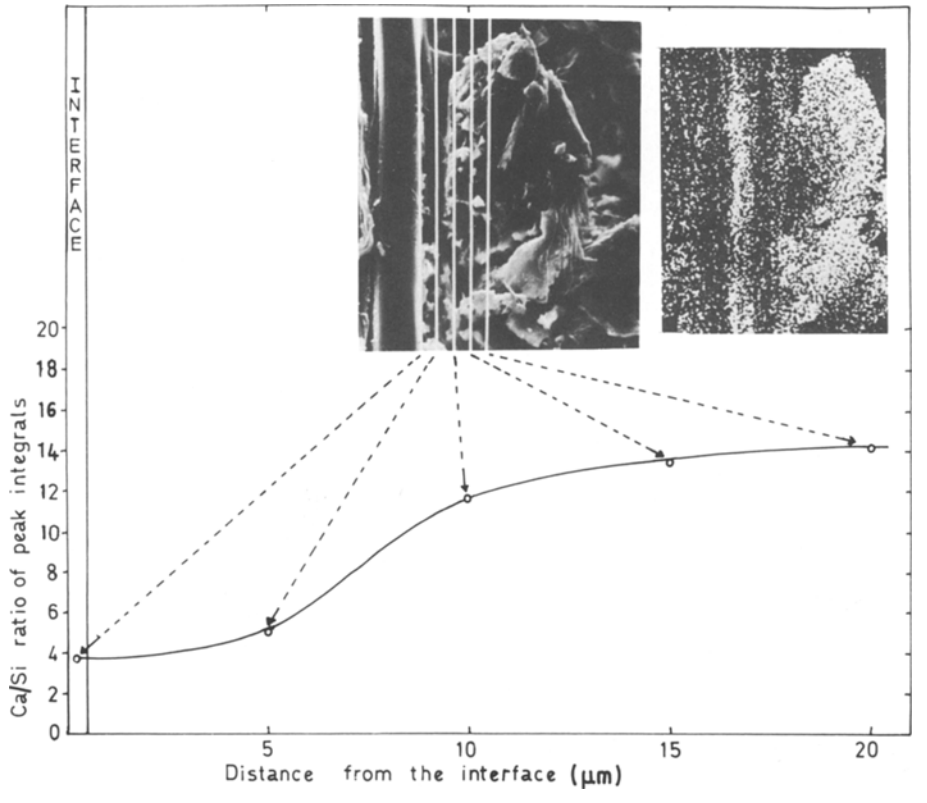


Figure 7 Local increases in the Ca/Si ratio, as determined by line scan analyses away from the interface, due to the presence of a calcium hydroxide crystal, identified by its high calcium content (see insets at magnification X 430).

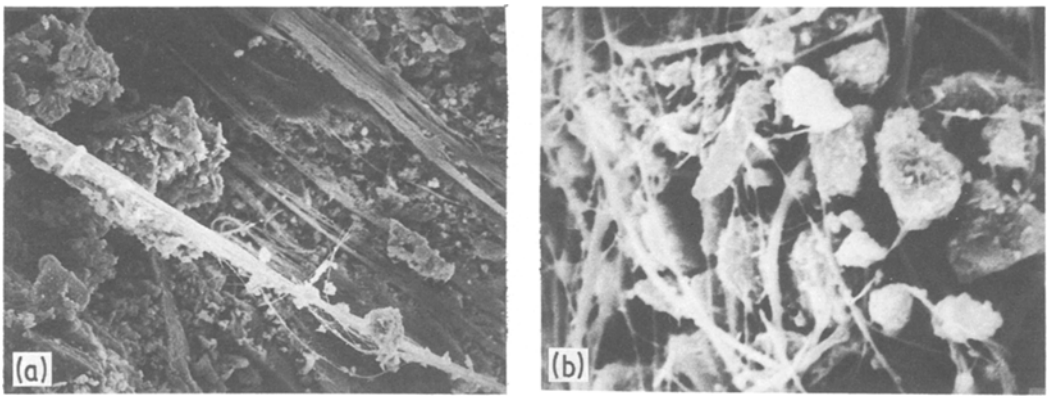


Figure 8 (a) Chrysotile fibrils remaining in a cement trough after pull-out. At higher magnification (b) the complex interaction between these fibrils and the cement particles is clearly illustrated.

turally weaker zone adjacent to the interface enriched in calcium hydroxide, as has been reported for other cement-based fibre composites [4, 10]. The reasons for this difference in behaviour are worth pursuing, particularly with regard to finding a suitable alternative fibre to asbestos.

It has been reported [15] that a change in zeta potential of the fibres as a result of the fiberizing treatment may cause increased adsorption of water molecules to the fibre bundles. Coupled with the corresponding significant increase in fibre surface area available for water adsorption, one might reasonably expect some fairly uniform distribution of water-filled voids in the interfacial region and subsequent calcium hydroxide enrichment during the hydration process. The observed difference from other fibres, therefore, may be attributed firstly to differences in the physical characteristics of the fibres, since it has been suggested [16] that inertia effects can give rise to preferential pore formation at interfaces, at least for the case of steel fibres; and secondly, to differences in the processing treatment which involve a pressing operation in the case of asbestos–cement.

Since many of the specimens examined were found to have either a thin film of cement surrounding the fibre bundle, or relatively large amounts of cement adhering to the surface, it must be concluded that fracture generally occurs away from the interface, implying that a good interfacial bond is maintained, stronger in fact than in the cement matrix itself. The important implication of this, of course, is that attempts aimed to improve the strength of the composite must also be directed towards increasing the strength of the cement matrix, since this would appear to be a limiting factor for a given fibre distribution.

However, a more detailed and statistical evaluation of the mechanism of debonding has shown that this would appear to be more complex than merely a separation of matrix and fibre at, or more generally, adjacent to the interface. Thus, single fibre bundles ($\sim 100\,\mu$m in diameter and ~ 25 mm long), which had been carefully cut from parent silicate rock and the ends subsequently cast into two separate pellets, were pulled out by loading through the end pellets. Scanning electron microscopy of sections cut through the length of the cylindrical pellet after pull-out revealed traces of fibrils in the trough from which the fibre bundle had been extracted.

An example of this is shown in Fig. 8a. A higher magnification fractograph of a typical trough, Fig. 8b, illustrates the complex manner in which the fibrils interact with cement particles, as has been discussed previously. Fig. 9a shows how a sheath of fibrils has separated from the extracted chrysotile fibre bundle. This separation of the sheath from the main core could clearly be seen when observing (with the aid of an optical microscope) the section of the fibre bundle outside the pellet caps during pull-out: the sheath separates from the fibre bundle at a distance outside the cement cylinder, Fig. 9b.

From these observations of the nature and behaviour under load of the interfacial region of chrysotile fibres in a cement matrix, it is evident that debonding and fibre pull-out in asbestos–cement involves a complex combination of failure mechanisms. The value of the interfacial shear stress, therefore, must be regarded as arising from

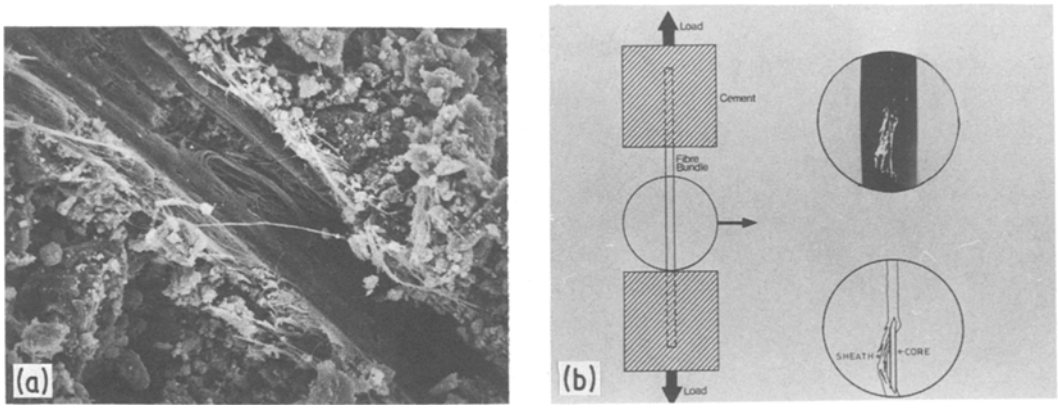


Figure 9 (a) A full sheath of chrysotile fibres remaining in a cement trough, after the bulk of the particular fibre bundle has been pulled out. (b) The mechanism of this separation observed with optical microscopy on a single fibre bundle pull-out specimen, illustrating the sheath shedding from the inner core as load is applied.

a combination of both interfacial debonding, primarily through matrix failure adjacent to the interface, and interfibre separation. The magnitude of the latter failure mode, whether it involves a distinct sheath or many tiny fibrils which remain attached to the matrix, is likely to be dependent on the mechanical treatment the fibre bundles have received before they are added to the cement matrix.

5. Conclusions

1. An important mechanism of interfacial bonding in asbestos–cement composites involves a mutual interlocking of asbestos fibres with a needle-like cement hydrate morphology of similar dimensions. Mechanical strength improvements can be obtained under conditions appropriate for optimized interlocking (water curing and well-opened fibre bundles).

2. Fractographic studies have indicated that many fibre bundles have cement adhering to the surface, suggesting that failure occurs adjacent to, as opposed to at, the interface. Energy dispersive X-ray measurements show no evidence of a calcium hydroxide-enriched zone (of mechanical weakness) adjacent to the interface, as has been reported for other cement-based fibre composites. The fibre–matrix bond strength would therefore appear to exceed that of the cement matrix itself, such that any future improvements could be limited by inherent matrix strength.

3. Composite strength will also be influenced by the interfibre bonding existing within fibre bundles, since direct observations have also shown the existence of mechanical separation of fibre cores from outer sheaths during pull-out.

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